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Fist oxidovanadium complexes containing chiral derivatives of dihydrophenanthroline and diazafluorene

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ABSTRACT

Reactions of VCl_3 with chiral derivatives of dihydrophenanthroline (2*R*,4*R*,9*R*,11*R*)-3,3,10,10-tetramethyl-1,2,3,4,6,7,9,10,11,12-decahydro-2,4:9,11-dimethanodibenzo[*b*,*j*][1,10]phenanthroline (**L1**) and diazafluorene (1*R*,3*R*,8*R*,10*R*)-2,2,9,9-tetramethyl-2,3,4,7,8,9,10,12-octahydro-1*H*-1,3:8,10-dimethanocyclopenta[1,2-*b*:5,4-*b*′]diquinoline (**L2**) in acetonitrile in air yield mixtures of $[V^{III}(\mathbf{L1}/\mathbf{L2})(CH_3CN)Cl_3]$ and $[V^{IV}O(\mathbf{L1}/\mathbf{L2})(CH_3CN)Cl_2]$ (**I**, **II**) which were characterized by elemental analysis, IR spectroscopy and magnetic susceptibility data. The behavior of these mixtures in different solvents was investigated by ^{51}V NMR and EPR spectroscopies as well as optical rotation. Recrystallization of a $[V^{III}(\mathbf{L1})(CH_3CN)Cl_3]/[V^{IV}O(\mathbf{L1})(CH_3CN)Cl_2]$ mixture from CH_2Cl_2/Et_2O affords a V(IV) complex, $[V^{IV}O(\mathbf{L1})(H_2O)Cl_2]\cdot n CH_2Cl_2$ (**III**). Recrystallization from $MeOH/Et_2O$ leads to complete oxidation to V(V) complex $[V^{V}O(\mathbf{L1})(OMe)Cl_2]$ (**IV**), which was characterized by X-ray crystallography, IR, ^{51}V and ^{1}H NMR spectroscopies.

1. Introduction

Oxido complexes containing the V^{IV}═O and V^{V}═O moieties are ubiquitous in the coordination chemistry of vanadium [1]. They demonstrate efficient catalytic oxidase reactivity in various transformations such as olefin epoxidation [2], aromatization of α,β-unsaturated cyclohexanone derivatives [3], alcohol oxidation [4], C—C bond cleavage of glycols to give the corresponding ketones [5], naphthol coupling [6], and α-oxidation of hydroxyl esters and amides [7]. In addition, they are part of vanadium-dependent haloperoxidases [8,9].

N-donor ligands play an important role in the chemistry of vanadium oxido complexes. In particular, much attention received the complexes with Schiff bases (N- or N, O-donor bi- or tetradentate ligands) that exhibit biological activity and catalytic properties in various oxidation reactions [2,10].

A separate group is vanadium oxido complexes with N-donor heterocyclic diimines (2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and their derivatives). In particular, binuclear complexes $[(VO)_2(L)_2(bta)(H_2O)_2]$ (L = bpy, phen; H_4bta = 1,2,4,5-benzenetetracarboxylic acid) catalyze the conversion of phenol red to bromophenol blue in the presence of H_2O_2 and Br^-, which mimics vanadium-dependent haloperoxidases [11]. Among mononuclear complexes, bis-substituted complexes with general formula *cis*-$[V^{IV}O(X)(L)_2]^+$ (X = OH^-, Cl^-, SO_4^{2-}, F^-; L = bpy, phen and their derivatives) are the most common [12,13]. The *cis*-$[V^{IV}OF(dbbpy)_2]ClO_4$ complex (dbbpy = 4,4′-di-tert-butyl-2,2′-bipyridine) with mainly ionic V—F bond can be used as a fluorinating agent and can convert quantitatively°, for example, $(CH_3)_3Si$-Cl to $(CH_3)_3SiF$ [13]. Oxido complexes with only one diimine ligand are less common. There are some mixed-ligand complexes, for example, $[V^{IV}O(sal\text{-}mdtc)(bpy)]$, $[V^{IV}O(sal\text{-}mdtc)(phen)]$ (sal-mdtcH_2 = salicylaldehyde S-methyldithiocarbazone) [14], $[V^{IV}O(bpy)(H_2cit)]2H_2O$, $[V^{IV}O(Hmal)(bpy)]H_2O$ and $[V^{IV}O(H_2cit)(phen)]1.5H_2O$ (H_4cit = citric acid; H_3mal = R,S-malic acid) [15]. The oxido complexes of vanadium(V) include oxido-peroxido derivatives such as $[V^{V}O(O_2)(pca)(bpy)]$ and $[V^{V}O(O_2)(pca)(phen)]$ (pca = 2-pyrazinecarboxylic acid) [16], dioxido derivatives such as $[V^{V}O_2(dbbpy)_2](BF_4)$ [17] and a dinuclear complex $[(V^{V}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}SO_4)(dbbpy)_2]$ [18]. Vanadium oxido complexes with chiral diimine ligands are still unknown.

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